

Preparation of Some Polymerizable Esters of Oleic Acid with Unsaturated Alcohols

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In recent years considerable attention has been directed to the preparation of unsaturated compounds suitable for use as monomers in polymerization reactions. Most of the published work, however, has described the preparation and properties of short-chain compounds, whereas long-chain compounds, derivable from fats and oils, have been the subject of relatively few investigations. We have been concerned for some time with the preparation and utilization of purified oleic acid,² and this report describes the preparation, physical properties and polymerization of eight unsaturated alcohol esters of oleic acid, namely, vinyl, allyl, 2-chloroallyl, methallyl (2-methylallyl), crotyl, 3-buten-2-yl (1-methylallyl), furfuryl and oleyl oleate.

No reference to the preparation of 2-chloroallyl, methallyl, crotyl, and 3-buten-2-yl oleate could be found in the literature. Oleyl oleate, which is reported to be a component of sperm blubber oil,^{3a} has been described by Meyer and Lühdemann^{3b} and by Sauer and Adkins,^{3c} but the purity of the product is questionable. Several workers have described the preparation of allyl oleate,⁴ but numerous discrepancies exist in the reported physical properties of this compound. The preparation of vinyl oleate has been reported in patents,⁵ but the purity of neither the oleic acid nor the ester obtained was given. The boiling point of the product was the only property reported. The preparation of furfuryl oleate has been described,⁶ but no properties were reported.

The allyl, 2-chloroallyl and oleyl esters were prepared by esterification of oleic acid with the appropriate alcohol, with naphthalene-2-sulfonic acid as a catalyst and benzene as an entraining agent to remove the water formed during the reaction.⁷ The methallyl, crotyl, 3-buten-2-yl and furfuryl esters were prepared by alcoholysis of methyl oleate with the appropriate alcohol, the corresponding sodium alcoholate being used as catalyst.⁸ Vinyl oleate was prepared by acidolysis

of vinyl acetate with oleic acid, in the presence of mercuric acetate and sulfuric acid as catalysts.^{8b} The yields of esters were very good. With the exception of furfuryl oleate which is pale-yellow, the esters are colorless, odorless, high-boiling liquids. They are relatively stable and may be stored for long periods in a nitrogen atmosphere without any apparent change, and with the exception of oleyl oleate, which was not distilled because of its extremely high boiling point, they yield small residues of thermopolymers on vacuum distillation (pot temperatures, 200–230°). The results are summarized in Table I. The low iodine number and high saponification number of vinyl oleate are attributed to the abnormal reactivity of vinyl compounds with the analytical reagents.

Small samples of each of the esters were heated to 100° in an atmosphere of nitrogen with 1% of benzoyl peroxide, and the refractive index was determined at frequent intervals. The change in refractive index with time, as well as its increment over the entire time interval studied, is shown in Fig. 1. Vinyl and 2-chloroallyl oleates, which one would predict to be the most reactive of the oleates in peroxide-catalyzed polymerizations, showed the greatest increase in refractive index. These compounds became noticeably more viscous as the polymerization progressed, and at the end of the reaction period they were insoluble in acetone and glacial acetic acid. The 2-chloroallyl oleate product was light brown. Oleyl, crotyl and furfuryl oleates displayed the smallest increase in refractive index, as would be expected. Allyl, methallyl and 3-buten-2-yl oleates were intermediate in reactivity. All the curves have one feature in common, namely, a rapid initial rise in refractive index followed by a relatively long period of time in which the refractive index remains substantially constant. 2-Chloroallyl, vinyl, methallyl, allyl and 3-buten-2-yl oleates, however, undergo an additional increase in refractive index, which is not shown by the other esters. We have no explanation for this phenomenon, but it should be noted that these five esters are the most reactive.

Although it is obvious that the esters of oleic acid are much less reactive than homologous, short-chain compounds, thus indicating that they (the oleates) would find little utility as the sole monomers in polymerization reactions, we were also interested in determining whether these esters would co-polymerize readily with a highly reactive unsaturated monomer, such as vinyl acetate. Our interest in such a reaction was two-fold. First, we wished to determine whether insoluble, infusible products could be obtained, in order to be able to state that the 9,10-double bond in oleic

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

(2) Swern, Billen, Findley and Scanlan, *THIS JOURNAL*, **67**, 1786 (1945); Swern, Scanlan and Roe, *Oil & Soap*, **23**, 128 (1946). Consult these papers for previous references.

(3) (a) Hilditch, "The Chemical Constitution of Natural Fats," John Wiley & Sons, Inc., N. Y., 1940, pp. 53 and 231; (b) Meyer and Lühdemann, *Helv. Chim. Acta*, **18**, 307 (1935); (c) Sauer and Adkins *THIS JOURNAL*, **59**, 1 (1937).

(4) Koyama, *J. Chem. Soc. Japan*, **52**, 768 (1931); Plisov and Golendeev, *Rept. U. S. S. R. Fat Margarine Inst.*, **2**, 3 (1935); Golendeev, *J. Gen. Chem., U. S. S. R.*, **10**, 1539 (1940).

(5) (a) Reppe, German Patent 588,352 (1933); U. S. Patent 2,066,075 (1936); (b) Toussaint and MacDowell, Jr., U. S. Patent 2,299,862 (1942).

(6) Norris and Terry, *Oil & Soap*, **21**, 193 (1944).

(7) Swern and Jordan, *THIS JOURNAL*, **67**, 902 (1945).

(8) Swern, Jordan and Knight, *ibid.*, **68**, 1673 (1946).

TABLE I

R	Formula	Yield, ^a %	B. p., °C.	°C. Mm.	Iodine no. (Wijs, 1 hr.)		Sapon. no.		Carbon, %		Hydrogen, %		n_D^{20} (Abbe)	d_4^{20}	Molecular refraction	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found			Calcd.	Found
Vinyl	$\text{C}_{19}\text{H}_{34}\text{O}_2$	64	178	2.8	164.5	159.0	181.9	190.0	77.8	77.7	11.8	12.1	1.4533	0.8691	95.3	95.9
Allyl	$\text{C}_{21}\text{H}_{38}\text{O}_2$	92	199-200	5	157.3	156.5	173.9	174.4	78.2	78.6	11.9	12.4	1.4539	0.8696	99.9	100.4
2-Chloroallyl ^c	$\text{C}_{21}\text{H}_{37}\text{O}_2\text{Cl}$	80	216	5	70.7	71.1	1.4627	0.9318	104.8	105.5
Methallyl (2-methylallyl)	$\text{C}_{20}\text{H}_{36}\text{O}_2$	75	203-205	4.3	150.7	149.5	166.8	168.0	78.6	79.2	12.0	11.5	1.4546	0.8679	104.5	105.1
Crotyl	$\text{C}_{20}\text{H}_{36}\text{O}_2$	79	203	3.5	150.7	149.9	166.8	167.6	78.6	78.5	12.0	12.4	1.4556	0.8693	104.5	105.0
3-Buten-2-yl (1-methyl- allyl)	$\text{C}_{20}\text{H}_{36}\text{O}_2$	76	193-194	3.5	150.7	151.4	166.8	168.3	78.6	78.2	12.0	12.0	1.4504	0.8628	104.5	104.8
Furfuryl	$\text{C}_{22}\text{H}_{38}\text{O}_3$	68	195	0.1	154.8	155.9	76.2	75.9	10.6	10.7	1.4681	0.9295	108.1	108.6
Oleyl	$\text{C}_{27}\text{H}_{50}\text{O}_2$	80	95.2	92.2	105.2	104.8	81.2	81.3	12.9	13.2	1.4605	0.8600	169.2	169.8

^a Purified products after two vacuum distillations. Oleyl oleate was purified by low-temperature fractional crystallization. ^b Analyses by Mary Jane Welsh of this Laboratory. ^c Anal. for chlorine: calcd., 9.93; found, 10.1.

acid is capable (or incapable) of entering typical olefinic copolymerization reactions⁹; second, we hoped to prepare polymers in which a long fatty acid chain was an actual part of the polymer molecule and to determine what effect this would have on the polymer produced. It has long been known that the mechanical admixture of fatty compounds with polymeric materials markedly affects the properties of the resulting products. However, fatty compounds often suffer from the disadvantages of low compatibility with many high-polymeric substances, and if they are compatible, they tend to exude from the material

upon handling, thereby imparting an undesirable "greasy feel." We believed that if the fatty compound under consideration was chemically bound in the polymer, these disadvantages would no longer be present. The greatest difficulty in the past in making fatty compounds an integral part of the polymer molecule in olefin co-polymerizations has been the unavailability of pure fatty derivatives having the necessary functional groups.

Solutions of freshly distilled vinyl acetate containing from 1% to 40% of the oleate esters (on a total monomer basis) were polymerized, as described by Guile and Huston,¹⁰ with 0.5% of ben-

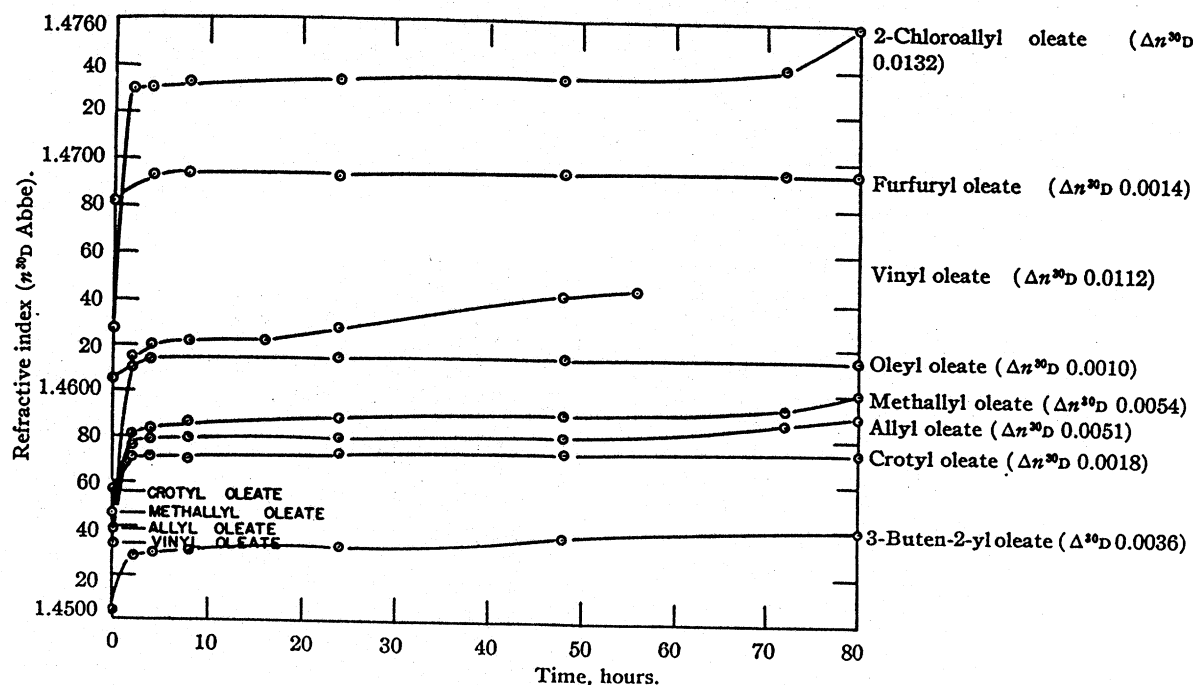


Fig. 1.—Refractive index plotted against time of polymerization of unsaturated alcohol esters of oleic acid (1% benzoyl peroxide as catalyst, 100°).

(9) Unsaturated esters of long-chain saturated acids, such as vinyl myristate, yield soluble co-polymers with vinyl acetate (unpublished results).

(10) Guile and Huston, "A Revised Laboratory Manual of Synthetic Plastics and Resinous Materials," Michigan State College, 1944, p. 99.

zoyl peroxide as catalyst. The co-polymers obtained ranged in physical appearance from hard, glass-like resins to tough, elastic gels or viscous oils. The results are summarized in Table II.

TABLE II
CO-POLYMERIZATION OF VINYL ACETATE AND ESTERS OF
OLEIC ACID WITH 0.5% BENZOYL PEROXIDE AS CATALYST

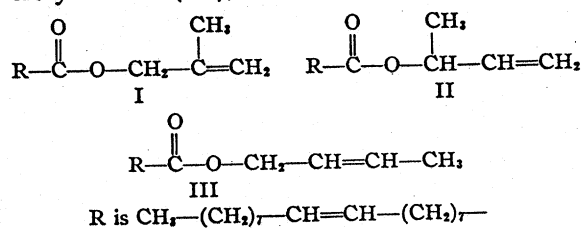
Monomer mixture Vinyl acetate, % ^a	Ester, % ^a	Solu- bility ^a	Physical appearance
2-Chloroallyl oleate			
100	0	S	Hard, glass-like, colorless
99	1	I	Tough, hard, colorless
91	9	I	Tough, hard, colorless
80	20	I	Tough, pliable, colorless
70	30	I	Tough, pliable, colorless
60	40	I	Tough, soft, colorless
Vinyl oleate			
99	1	I	Tough, hard, colorless
91	9	I	Tough, pliable, colorless
80	20	I	Tough, soft, colorless
70	30	I	Soft, elastic, colorless
60	40	S	Viscous liquid, colorless
Methallyl oleate			
99	1	I	Hard, glass-like, colorless
91	9	I	Tough, hard, colorless
80	20	I	Tough, soft, colorless
70	30	I	Soft, elastic, colorless
60	40	S	Slightly viscous liquid, colorless
Allyl oleate			
99	1	I	Tough, hard, colorless
91	9	I	Tough, soft, colorless
80	20	I	Very soft, elastic, colorless
70	30	S	Viscous liquid, colorless
60	40	S	Viscous liquid, colorless
3-Buten-2-yl oleate			
99	1	I	Hard, glass-like, colorless
91	9	I	Tough, pliable, colorless
80	20	I	Soft, elastic, colorless
70	30	S	Very soft, elastic, colorless
60	40	S	Viscous liquid, colorless
Crotyl oleate			
99	1	S	Hard, glass-like, colorless
91	9	S	Soft, elastic, colorless
80	20	S	Very soft, elastic, colorless
70	30	S	Heterogeneous: viscous and non-viscous liquids, colorless
60	40	S	Heterogeneous, viscous and non-viscous liquids, colorless
Furfuryl oleate			
99	1	S	Hard, glass-like, straw yellow
91	9	S	Hard, glass-like, straw yellow
80	20	S	Viscous liquid, light brown
70	30	S	Viscous liquid, light brown
60	40	S	Viscous liquid, light brown

Oleyl oleate			
99	1	S	Hard, glass-like, colorless
91	9	S	Heterogeneous: non-viscous liquid and tough, hard polymer, colorless
80	20	S	Heterogeneous: non-viscous liquid and tough, hard polymer, colorless
70	30	S	Heterogeneous: non-viscous liquid and tough, hard polymer, colorless
60	40	S	Heterogeneous: non-viscous liquid and tough, hard polymer, colorless

^a S = Soluble in acetone, amyl acetate and acetic acid at room temperature. I = insoluble in boiling acetone, and in amyl acetate and acetic acid at 100°.

Over the entire percentage range studied, the most reactive ester, namely, 2-chloroallyl oleate, yielded insoluble co-polymers. Vinyl, methallyl, allyl and 3-buten-2-yl oleates also yielded insoluble co-polymers, provided that they did not exceed about 30, 30, 20 and 20%, respectively, of the total monomers used. Co-polymers containing up to 40% of 2-chloroallyl oleate were insoluble gels which charred without melting when heated on a spatula over an open flame. Likewise, co-polymers containing up to about 30% vinyl oleate, 30% methallyl oleate, 20% allyl oleate or 20% 3-buten-2-yl oleate behaved similarly. When squeezed in thin layers between sheets of absorbent paper these gels did not exude any fatty material, indicating that the oleate esters were probably entirely chemically bound. The products containing crotyl, furfuryl and oleyl oleates were soluble in organic solvents. This is to be expected, since the reactivity of these three esters is considerably lower than that of the five esters which yielded insoluble products.

The data in Table II indicate that the 9,10-double bond in oleic acid is capable of entering a typical olefinic co-polymerization reaction, although such a reaction proceeds slowly. If it proceeded rapidly, oleyl oleate would have yielded an insoluble, cross-linked co-polymer with vinyl acetate. It should also be noted that the cross-linking tendencies, as well as the rates of polymerization, of the three isomeric butenyl oleates, namely, methallyl (I), 3-buten-2-yl (II), and crotyl oleates (III), decrease in the order named.



Experimental

Starting Materials.—Allyl, 2-chloroallyl, methallyl, crotyl, 3-buten-2-yl and furfuryl alcohols were the purest commercial grades, and they were distilled before use through an efficient fractionating column. Vinyl acetate was the purest commercial grade (stabilized with copper resinate and diphenylamine), and it was fractionally distilled in an apparatus completely shielded from light. It

was used as soon as it was purified. Oleyl alcohol was prepared as previously described and contained less than 0.1% of polyunsaturated alcohols.¹¹ The oleic acid and methyl oleate, prepared from olive oil by slight modifications of well-known methods,^{11,12,13} contained less than 0.2% of polyunsaturated components.

Esterification Procedures.—Allyl, 2-chloroallyl and oleyl oleates were prepared by esterification of oleic acid with the appropriate alcohol, which was employed in a 100, 100 and 2% molar excess, respectively, with 1–2% of naphthalene-2-sulfonic acid (based upon the oleic acid) as catalyst and benzene as an entraining agent to remove the water formed during the reaction.⁷ About three to five hours were required to obtain the theoretical quantity of water. In the preparation of the allyl ester, a six-plate fractionating column was employed to separate the benzene–water azeotrope from the unreacted allyl alcohol. After completion of the reactions, a slight excess of sodium bicarbonate over that required to neutralize the catalyst was added, and the benzene was recovered.

In the preparation of the allyl and 2-chloroallyl esters, the distillation was continued at atmospheric pressure until the major portion of the unreacted alcohol was recovered. The small amount remaining was removed under reduced pressure by means of a water aspirator. The residue of crude esters was distilled in an atmosphere of nitrogen through a 45-cm. Vigreux column, yielding fairly pure allyl and 2-chloroallyl oleates, b. p. 194–200° (5 mm.) and 206–214° (4.5 mm.), respectively, in more than a 90% yield. These products usually had an acid number of 2 to 6. They were redistilled after the addition of sufficient sodium bicarbonate to neutralize the free acid. The main fractions, as determined by boiling point and refractive index, were retained and stored under nitrogen.

The oleyl ester, after recovery of the benzene, was dissolved in Skellysolve B (10 ml. per gram) and filtered to separate insoluble salts, which were rejected. The filtrate was cooled to –60°, and the precipitate which formed consisted of fairly pure oleyl oleate. It was recrystallized from Skellysolve B at –60°. The occluded solvent was removed from the precipitate by distillation, the last traces under vacuum, yielding oleyl oleate as a residue.

Methallyl, crotyl, 3-buten-2-yl and furfuryl oleates were prepared by alcoholysis of methyl oleate with the desired alcohol, the corresponding sodium alcoholate being used as catalyst.⁸ A typical preparation is as follows: Metallic sodium (0.45 g.), cut into small pieces, was added slowly to 3.0 moles of the alcohol at room temperature. Methyl oleate (89 g., 0.3 mole) was added, and the solution was heated on the steam-bath (95–100°) in an atmosphere of nitrogen for three hours, with occasional shaking. The methyl alcohol formed during the reaction was permitted to escape. The major portion of the unreacted alcohol was distilled off at atmospheric pressure and the remainder at 40–50 mm. (furfuryl alcohol was recovered in its entirety at 40–50 mm.). The residue of crude esters was distilled through a 45-cm. Vigreux column, yielding a fairly pure product (80–90% yield); methallyl oleate, b. p. 193–206° (4.3 mm.); furfuryl oleate, 188–199° (0.1 mm.); crotyl oleate, 200–207° (3 mm.); 3-buten-2-yl oleate, 180–185° (2.2 mm.). These were redistilled and the main fractions, as determined by boiling point and refractive index, were retained and stored under nitrogen.

Vinyl oleate was prepared by the acidolysis of vinyl acetate with oleic acid in the presence of mercuric acetate and sulfuric acid as catalysts, according to the procedure of Toussaint and MacDowell.¹⁴ The crude vinyl oleate, b. p. 160–170° (1 mm.), obtained in 78% yield, was redistilled as described for the other esters.

The results are summarized in Table I.

Polymerization of Esters of Oleic Acid.—Small quantities of each of the esters were weighed into test-tubes which had been flushed with nitrogen, 1% of benzoyl peroxide was added and the tubes were again flushed with nitrogen and tightly stoppered. The tubes were immersed in a constant temperature oil-bath maintained at 100° ± 0.2, and small samples were withdrawn at intervals for refractive index measurement. The tubes were flushed with nitrogen after the removal of each sample. The results are shown in Fig. 1.

Co-polymerization of Esters of Oleic Acid with Vinyl Acetate.—In small test-tubes which had been flushed with nitrogen, freshly distilled vinyl acetate and the esters of oleic acid were mixed in the proportions shown in Table II and 0.5% of benzoyl peroxide (based upon the total monomer weight) was added. The tubes were again flushed with nitrogen and stoppered, and the co-polymerizations were conducted in a thermostatically controlled oven, as described by Guile and Huston.¹⁰ Solubilities of the resulting co-polymers were determined in amyl acetate and acetic acid both at room temperature and at 100°, and in acetone at room temperature and at its boiling point.

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Summary

Eight esters of oleic acid, namely, vinyl, allyl, 2-chloroallyl, methallyl (2-methylallyl), crotyl, 3-buten-2-yl (1-methylallyl), furfuryl and oleyl oleate have been prepared in good yield from oleic acid and methyl oleate, and some of their properties have been determined. They are stable, high-boiling liquids, and with the exception of oleyl oleate, which was not distilled because of its extremely high boiling point, they yield very small residues of thermopolymers on vacuum distillation (pot temperatures, 200–230°).

The polymerization of these esters at 100° in the presence of 1% of benzoyl peroxide as catalyst has been studied. Vinyl and 2-chloroallyl oleates polymerized at a much more rapid rate than any of the other esters, yielding viscous oils insoluble in acetone and glacial acetic acid, whereas crotyl, furfuryl and oleyl oleates polymerized only slightly. The other esters were intermediate in reactivity.

The co-polymerization of these esters with vinyl acetate in the presence of 0.5% of benzoyl peroxide as catalyst has also been studied. Over the entire percentage range investigated (maximum content of oleate, 40%) 2-chloroallyl oleate yielded co-polymers which were insoluble in organic solvents and which ranged from hard, glass-like resins to tough, rubbery gels. Vinyl, methallyl, allyl and 3-buten-2-yl oleates also yielded insoluble co-polymers, provided that they did not exceed about 30, 30, 20 and 20%, respectively, of the total monomers used.

The cross-linking tendencies, as well as the rates of polymerization, of the three isomeric butenyl oleates, namely, methallyl, 3-buten-2-yl and crotyl oleates, decrease in the order named.

(11) Swern, Knight and Findley, *Oil & Soap*, **21**, 133 (1944).

(12) Brown and Shinowara, *This Journal*, **59**, 6 (1937).

(13) Wheeler and Riemenschneider, *Oil & Soap*, **16**, 207 (1939).